

Nanoparticles of Block Ionomer Complexes from Double Hydrophilic Poly(acrylic acid)-*b*-poly(ethylene oxide)-*b*-poly(acrylic acid) Triblock Copolymer and Oppositely Charged Surfactant

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Abstract The novel water-dispersible nanoparticles from the double hydrophilic poly(acrylic acid)-*b*-poly(ethylene oxide)-*b*-poly(acrylic acid) (PAA-*b*-PEO-*b*-PAA) triblock copolymer and oppositely charged surfactant dodecyltrimethyl ammonium bromide (DTAB) were prepared by mixing the individual aqueous solutions. The structure of the nanoparticles was investigated as a function of the degree of neutralization (DN) by turbidimetry, dynamic light scattering (DSL), ζ -potential measurement, and atomic force microscope (AFM). The neutralization of the anionic PAA blocks with cationic DTAB accompanied with the hydrophobic interaction of alkyl tails of DTAB led to formation of core-shell nanoparticles with the core of the DTAB neutralized PAA blocks and the shell of the looped PEO blocks. The water-dispersible nanoparticles with negative ζ -potential were obtained over the DN range from 0.4 to 2.0 and their sizes depended on the DN. The looped PEO blocks hindered the further neutralization of the PAA blocks with cationic DTAB, resulting in existence of some negative charged PAA-*b*-PEO-*b*-PAA backbones even when DN > 1.0. The spherical and ellipsoidal nature of these nanoparticles was observed with AFM.

Keywords Nanoparticles · Block ionomer complexes · Water-dispersible · Double hydrophilic triblock copolymer · Surfactant

Introduction

The double hydrophilic block copolymers containing ionic and nonionic water-soluble blocks (block ionomers) constitute a very active field in recent years for their unique aggregation behavior in aqueous solution [1, 2]. They exhibit the solution behavior of normal polyelectrolyte in aqueous solutions, while the amphiphilicity can be induced by changing pH or complexing with oppositely charged species (counterions, polyelectrolyte, or surfactants), which results in formation of nanoscale micelles, colloids, and vesicles [3–13]. Recently, a novel type of polymer-surfactant complexes formed by the block ionomers with the oppositely charged surfactant, called block ionomer complexes (BIC), has received increasing attention for current and potential applications in drug and gene delivery [12–25].

Kabanov and coworkers [12–17] first prepared the nano-sized BIC using a double hydrophilic poly(ethylene oxide)-*b*-poly(sodium methacrylate) (PEO-*b*-PMAA) diblock copolymer and various single-, double- and triple-tail cationic surfactants. The micelles or vesicles can be formed depending on length of the PMAA and PEO blocks in PEO-*b*-PMAA and structure of the surfactants. These complexes formed a stable aqueous dispersion and exhibited combined properties of amphiphilic block copolymers and polyelectrolyte-surfactant complexes [12–14]. Another type of BIC was formed between cationic PEO-*g*-poly(ethyleneimine) (PEO-*g*-PEI) copolymer and anionic alkyl sulfates [18] or sodium salt of oleic acid [19]. The water-dispersible micelle-like aggregates with a hydrophobic core of surfactant

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neutralized PEI chains and a hydrophilic corona of PEO chains were obtained over the whole range of composition. Li and Nakashima [20] prepared the water-dispersible nanoaggregates with the size ranging from 80 to 200 nm from PEO-*b*-PMAA by binding the cationic surfactant cetyltrimethylammonium chloride (CTAC). They also demonstrated the formation of the PEO-*b*-PMAA nanoaggregates with the size ranging from 50 to 200 nm through binding with cationic anesthetics [21]. Recently, they fabricated a micelle-like nanoaggregates with the size of 125 to 193 nm using the neutralization of PEO-*b*-poly(sodium 2-acrylamide-2-methylpropanesulfonate)-*b*-PAA (PEO-*b*-PAMPS-*b*-PAA) triple hydrophilic block copolymer by CTAC [22]. The electrostatic self-assembly of the poly(sodium acrylate)-*b*-poly(acrylamide) (PANA-*b*-PAM) diblock copolymer with cationic surfactant dodecyltrimethyl ammonium bromide (DTAB) led to formation of stable 100 nm of colloidal complexes with a core-shell structure. The core was constituted of dense packed DTAB micelles connected by the PANA chains, and the shell formed by PAM chains [23]. Spherical and ellipsoid shaped BIC was also produced by reacting the sodium (sulfamate-carboxylate) isoprene/ethylene oxide (SCIEO) double hydrophilic diblock copolymer with DTAB [24]. In all these cases, the charged head groups of the surfactant were bound to the oppositely charged segments of the polyion blocks, resulting in formation of the hydrophobic core of nanoscale BIC, while the nonionic water-soluble block (e.g., PEO) formed the shell to prevent macroscopic phase separation [12, 13]. In contrast to the conventional polyelectrolyte-surfactant complexes, which precipitate from aqueous solution, the BIC are stable and soluble in aqueous dispersion over the entire range of composition, including stoichiometric complexes [12–24]. Alternatively, the comb-type or random hydrophilic copolymers may be used to produce the water-soluble complex with similar structure of BIC [25–29].

In this work, we tried to fabricate a novel type of water-dispersible BIC using the double hydrophilic poly(acrylic acid)-*b*-poly(ethylene oxide)-*b*-poly(acrylic acid) (PAA-*b*-PEO-*b*-PAA) triblock copolymer and cationic surfactant DTAB. The BIC formed the core-shell structure nanoparticles with the core consisting of the DTAB neutralized PAA blocks and the thin shell of looped PEO blocks. The looped PEO blocks in the shell hindered the further neutralization of the PAA blocks with cationic DTAB, resulting in that the zeta-potential of the nanoparticles remained negative over the whole DN range. The PAA-*b*-PEO-*b*-PAA triblock copolymer with well-defined structure was synthesized via ATRP of *tert*-butyl acrylate (*t*-BA) and followed by selective acidolysis of the *Pt*BA block. The nanoparticles of PAA-*b*-PEO-*b*-PAA were formed by binding oppositely charged surfactant (DTAB) in aqueous solution has been investigated using

turbidimetry, dynamic light scattering (DSL), zeta-potential, and atomic force microscope (AFM).

Experimental

Materials

Poly(ethylene oxide)-based ATRP macroinitiator Br-PEO-Br was synthesized through quantitative esterification of PEO ($M_n = 10,000$, Sinopharm Group Chemical Reagent Co.) with 2-bromoisobutyryl bromide in the presence of triethylamine following a reported procedure [30]. 2-Bromoisobutyryl bromide (98%), *N,N,N',N'',N''*-penta-methyl diethylenetriamine (PMDETA, 99%), trifluoroacetic acid (CF_3COOH , 99%), and pyrene (98%) purchased from Aldrich were used as received. *tert*-Butyl acrylate (*t*BA, 98%, Fluka) was passed through a basic alumina column to remove the inhibitor, and then distilled under reduced pressure before polymerization. Cu(I)Br was washed with pure acetic acid, absolute ethyl alcohol, and anhydrous ethyl ether, and then dried in vacuum at room temperature. Dodecyltrimethyl ammonium bromide (DTAB) was purchased from Beijing Chemical Reagents Co. Water was purified with a Milli-Q purification system after distillation.

Synthesis of PAA-*b*-PEO-*b*-PAA Triblock Copolymer

The PAA-*b*-PEO-*b*-PAA triblock copolymer was synthesized via ATRP of *t*BA initiated by the Br-PEO-Br macroinitiator and selective acidolysis of the *Pt*BA block. Br-PEO-Br (3.09 g, 0.3 mmol) and Cu(I)Br (0.0864 g, 0.6 mmol) were added in a 50-mL round-bottom flask under argon atmosphere, which was then sealed with a rubber septum. Deoxygenated toluene (8 mL) and *t*BA monomer (4 mL, 27.6 mmol) were introduced into the flask via an Ar-washed syringe. The mixture was stirred until the Br-PEO-Br macroinitiator was totally dissolved and then three freezing-pump-thaw cycles were performed to remove trace of oxygen in the system. After degassing, 125 μ L (0.6 mmol) of PMDETA was injected into the flask using an Ar-washed syringe under continuous stirring until the system became homogeneous. The reaction mixture was stirred at 80 °C for 6 h, and then the reaction was terminated by rapid cooling in liquid nitrogen. The crude product was dissolved in THF and passed through a basic alumina column to remove the catalyst, and then precipitated in a large excess of ether. The triblock copolymer *Pt*BA-*b*-PEO-*b*-*Pt*BA was obtained by drying in vacuum at room temperature (5.2 g, 79% yield).

Subsequently, hydrolysis was performed by adding excess of trifluoroacetic acid (CF_3COOH , five-fold molar

excess of the *t*-butyl group) to the *PtBA-b-PEO-b-PtBA* triblock copolymer solution (2.84 g, $C \sim 150$ g/L) in methylene chloride at 0 °C under vigorous stirring. The reaction was kept at 0 °C for 3 h and then at room temperature for 24 h. The solvent and residual CF_3COOH were removed by evaporation. The product was washed several times with ether to completely remove trace CF_3COOH . The *PAA-b-PEO-b-PAA* block copolymer was filtered and dried in vacuum at room temperature (2.25 g, 98% yield).

The compositions of the *PtBA-b-PEO-b-PtBA* and *PAA-b-PEO-b-PAA* triblock copolymers were determined by ^1H NMR spectroscopy using a Bruker Advance Digital 400 MHz NMR spectrometer in CDCl_3 and D_2O , respectively. The molecular weight M_n and molecular weight distribution index M_w/M_n of *PtBA-b-PEO-b-PtBA* triblock copolymer were determined with a gel permeation chromatography (GPC, Waters 2410) using THF as the eluent (1.0 mL/min) at 30 °C. The calibration curve was established using a set of narrowly distributed PS as the standard. The M_n and M_w/M_n of *PAA-b-PEO-b-PAA* triblock copolymer were determined with GPC using aqueous solution of 0.1 M Na_2SO_4 as the eluent (0.6 mL/min) at 25 °C. The calibration curve was established using a set of narrowly distributed PEO as the standard. The characterization results of the triblock copolymers are listed in Table 1. The copolymers are referred to as $\text{BA}_{31}\text{E}_{227}\text{BA}_{31}$ and $\text{AA}_{31}\text{E}_{227}\text{AA}_{31}$, where BA, E, and AA represent the *PtBA*, PEO, and PAA blocks, respectively, and the subscripts indicate the degree of polymerization of the corresponding block. The narrow distribution ($M_n/M_w = 1.06$) of *PtBA-b-PEO-b-PtBA* triblock copolymer reflects the feature of controlled radical polymerization of *tBA* initiated with the Br-PEO-Br macroinitiator via ATRP. The narrow distribution ($M_n/M_w = 1.15$) and well-defined structural *PAA-b-PEO-b-PAA* triblock copolymer was obtained by hydrolyzing this *PtBA-b-PEO-b-PtBA* triblock copolymer. The structure of the *PAA-b-PEO-b-PAA* (a) and DTAB (b) is shown in Fig. 1.

Table 1 Characterization of *PtBA-b-PEO-b-PtBA* and *PAA-b-PEO-b-PAA* copolymers

Samples ^a	M_n^b	M_w/M_n^b	$M_{n,\text{NMR}}^c$	DP ^c
$\text{BA}_{31}\text{E}_{227}\text{BA}_{31}$	25,700	1.06	18,250	62
$\text{AA}_{31}\text{E}_{227}\text{AA}_{31}$	15,460	1.15	14,760	62

^a BA, E, and AA represented the *PtBA*, PEO, and PAA blocks, the subscripts were the degree of polymerization of the *PtBA*, PEO, and PAA blocks, respectively

^b $\text{BA}_{31}\text{E}_{227}\text{BA}_{31}$ was determined by GPC in THF at 1.0 mL/min using PS as the standard; $\text{AA}_{31}\text{E}_{227}\text{AA}_{31}$ was determined by GPC in aqueous solution of 0.1 M Na_2SO_4 at 0.6 mL/min using PEO standards

^c Determined from ^1H NMR spectra

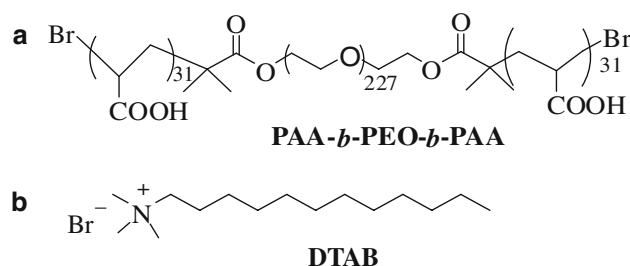


Fig. 1 Structure of *PAA-b-PEO-b-PAA* triblock copolymer (a) and DTAB (b)

Preparation of *PAA-b-PEO-b-PAA*/DTAB Nanoparticles

Stock solution of *PAA-b-PEO-b-PAA* was prepared by dissolving a weighed amount of the dialyzed *PAA-b-PEO-b-PAA* triblock copolymer in the appropriate volume of deionized water (Milli-Q). pH of the solution was adjusted to 9.0 using 1 mol/L of sodium hydroxide (NaOH) solution and the carboxylic groups in the *PAA-b-PEO-b-PAA* were completely ionized at pH 9.0. Concentrations in the range of 0.1 to 3.0 g/L were used for the copolymer. Surfactant DTAB was dissolved in deionized water (Milli-Q) to keep the concentration [DTAB] at 0.01 mol/L, which was lower than the nominal critical micelle concentration of DTAB in aqueous solution ($\text{CMC} = 20$ mM) [31], and no micelles formed by DTAB itself in the solution. The solutions were filtered through a hydrophilic Teflon Millipore membrane with pore size of 0.45 μm to remove dust.

The *PAA-b-PEO-b-PAA*/DTAB nanoparticles were prepared by adding different amounts of the DTAB solution to the triblock copolymer solution to realize designed degree of neutralization (DN) at constant volume and concentration under stirring. The DN was defined as the mole ratio of the added DTAB to the COO^- groups in the solution. Then, mixed solutions were adjusted to a constant final volume (5 mL) by adding additional volumes of deionized water. All mixed solutions were equilibrated for 24 h at room temperature.

Characterization

The transmittance T of the mixed solution was measured with a Hitachi UV-3010 UV/Vis spectrophotometer at 400 nm and 25 °C. The turbidity was calculated from T as $(100 - T)/100$. The solution was equilibrated for about 5 min prior to measurement.

The ζ -potential of the *PAA-b-PEO-b-PAA*/DTAB nanoparticles was measured at 25 °C with a Nano-ZS90 Zetasizer (Malvern Co.) equipped with a 22-mW He-Ne laser operating at $\lambda = 633$ nm. The apparent hydrodynamic

diameter D_h was determined with the photon correlation spectroscopy using the same instrument at 90° scattering angle. The CONTIN algorithm was adopted in the Laplace inversion of the autocorrelation function to obtain the size distribution of the nanoparticles. D_h was evaluated from the Stokes–Einstein equation as $R_h = kT/3\pi\eta D$, where k was the Boltzmann constant, T the absolute temperature, η the solution viscosity, and D the apparent diffusion coefficient. The solution was equilibrated for about 5 min before test.

An atomic force microscope (AFM, Seiko, SPA 400) was used to observe the nanoparticles in the tapping mode. Mixed solution (5 μ L) at DN = 1.0 was dropped on freshly cleaved mica. Water was allowed to evaporate from the grid at atmosphere pressure and 25 $^\circ$ C.

Results and Discussions

Solution Behavior of PAA-*b*-PEO-*b*-PAA/DTAB Nanoparticles

Turbidimetric titration was used to characterize the solubility of the PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles prepared at various DN. The turbidity measurement was performed at pH 9.0, at which the ionization of the PAA chains was practically complete. Figure 2 depicts the turbidity of the PAA-*b*-PEO-*b*-PAA/DTAB system as a function of DN, the concentrations of the triblock copolymer ($C_{\text{copolymer}}$) was kept as a constant of 1.0 g/L ($C_{\text{COO}^-} = 0.004$ mol/L). No macroscopic phase separation was observed for this system, and the mixed solutions were almost transparent in the whole DN range examined. The results suggest that the PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles remain soluble and form stable aqueous dispersions even at the isoelectric point (DN = 1.0). The transparent mixed solutions were obtained in the $C_{\text{copolymer}}$ range of 0.1 to 3.0 g/L. As known from the earlier studies by Kabanov and coworkers [12–14], the solution behavior of the BIC was strongly dependent on the length of the water-soluble non-ionic and ionic blocks. In the present case, the PAA-*b*-PEO-*b*-PAA triblock copolymer containing a long PEO block (DP = 226) and two short PAA blocks (DP = 31 for each) leads to the excellent solubility for the PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles in water. The nanoparticles are stable and no precipitate was observed after stored for several weeks. The turbidity of the PAA-PEO-PAA/DTAB system at high copolymer concentrations ($C_{\text{copolymer}} = 10, 20, 50$, and 100 g/L) at DN = 1.0 also was measured. The values of turbidity are 0.12, 0.24, 0.53 and 0.67 for the systems at $C_{\text{copolymer}} = 10, 20, 50$, and 100 g/L, respectively. A macroscopic phase separation was observed for the systems of $C_{\text{copolymer}} = 50$ and 100 g/L, and the solution became opalescent at DN = 1.0, indicating precipitation.

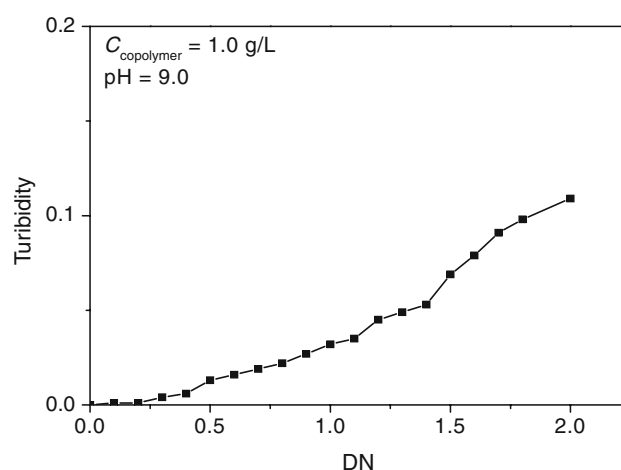


Fig. 2 Turbidity of the PAA-*b*-PEO-*b*-PAA/DTAB system as a function of DN at a copolymer concentration $C_{\text{copolymer}} = 1.0$ g/L

Size and ζ -Potential of the Nanoparticles

The PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles were characterized using the DSL and laser microelectrophoresis technique. Figure 3a shows the hydrodynamic diameter (D_h) distribution of the PAA-*b*-PEO-*b*-PAA/DTAB particles at various DN with a constant copolymer concentration $C_{\text{copolymer}} = 1.0$ g/L. Only one peak is observed and D_h increases with increasing DN, which confirms the formation of the nanoparticles. It should be noted that the concentration of DTAB in our case is much lower than its CMC (20 mM), DTAB should not form micelles itself. Figure 3b represents D_h and scattering intensity I_s of the PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles as a function of DN with a constant copolymer concentration $C_{\text{copolymer}} = 1.0$ g/L. When DN < 0.4, the count rate is too low and no aggregates can be determined by DSL, indicating that the nanoparticles formation begins at about DN = 0.4. D_h increases from 10.4 to 42.8 nm and I_s increases from 7.0 to 158 kcps upon increasing DN from 0.4 to 1.0, which indicates that the DTAB is bound to the ionized PAA block of the PAA-*b*-PEO-*b*-PAA copolymer to form the BIC and the size and number of the complex strongly depend on the added amount of DTAB in this DN range. D_h and I_s slightly increase in the DN range of 1.0 to 2.0, suggesting that the excess of DTAB (i.e., DN > 1.0) gives a negligible effect on the formation and size of the complex. The cationic head groups of the DTAB form salt bonds with the anionic carboxylate groups of the PAA-*b*-PEO-*b*-PAA, resulting in the hydrophobic alkyl tails of the DTAB grafted to the PAA blocks. This structure is similar to the amphiphilic ABA triblock copolymer composed of long hydrophilic B block and short hydrophobic A blocks [30]. As the nanoparticles are quite stable and the size is close to that of flowerlike micelles formed by amphiphilic

ABA triblock copolymers [30], it is reasonable to assume that they are core-shell aggregates as the flowerlike micelles formed by amphiphilic triblock copolymers. The neutralization of PAA blocks with charged groups of DTAB and the hydrophobic interaction of the alkyl tails of DTAB lead to formation of the hydrophobic cores, which are stabilized by the long loop of PEO blocks in aqueous medium. The size of the nanoparticles formed by the PAA-*b*-PEO-*b*-PAA/DTAB ($D_h \approx 43$ nm) is obviously smaller than that of the complex formed by the PEO-*b*-PMA/DTAB ($D_h \approx 94$ nm) [13]. The water-soluble PEO chains in the PEO-*b*-PMA diblock copolymer extend into the solution and form a thick shell in the previously reported PEO-*b*-PMA/DTAB system. The looped PEO blocks in the present PAA-*b*-PEO-*b*-PAA triblock copolymer form the thin shell of the nanoparticles.

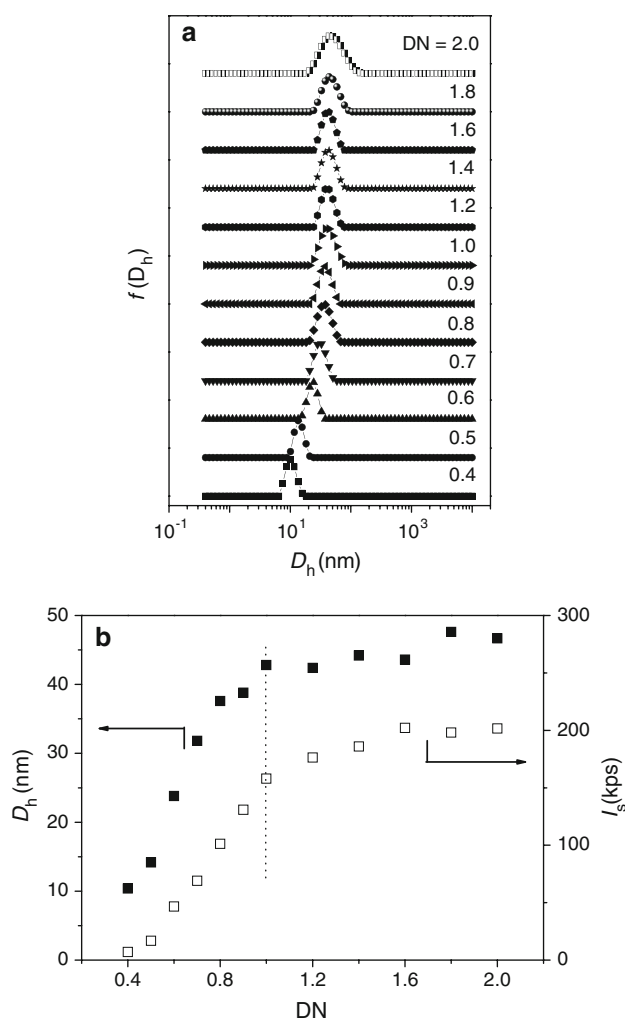


Fig. 3 The hydrodynamic diameter ($D_h = 2R_h$) distribution (a) and scattering intensity I_s (b) of the PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles at various DN with a copolymer concentration of $C_{\text{copolymer}} = 1.0$ g/L

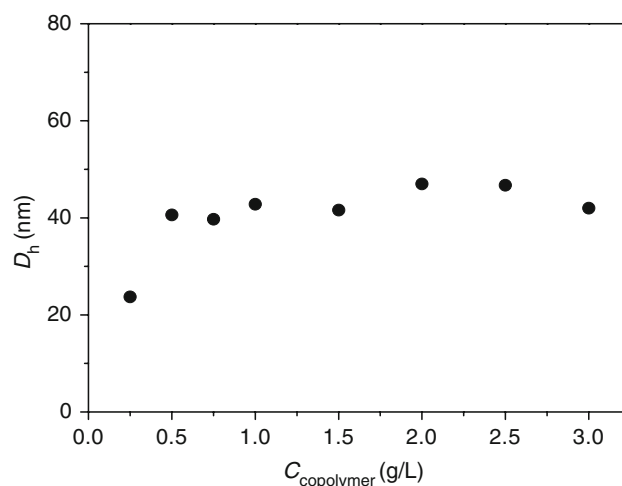


Fig. 4 Dependence of the D_h of the PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles on the PAA-*b*-PEO-*b*-PAA concentration ($C_{\text{copolymer}}$) at DN = 1.0

Figure 4 illustrates the dependence of the D_h of the PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles on the PAA-*b*-PEO-*b*-PAA concentration $C_{\text{copolymer}}$ at DN = 1.0. No aggregates can be detected when $C_{\text{copolymer}}$ is below 0.25 g/L. The D_h is nearly 24 nm at $C_{\text{copolymer}} = 0.25$ g/L, where formation of the PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles seems to begin. However, these nanoparticles were unstable and the D_h value increase after stored for several days. D_h of the nanoparticles is almost constant at 43 ± 3 nm and is unchanged for several weeks when $C_{\text{copolymer}}$ ranges from 0.5 to 3.0 g/L. The stable PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles were prepared by simply mixing the triblock copolymer with DTAB in aqueous medium in these $C_{\text{copolymer}}$ range. At high copolymer concentration ($C_{\text{copolymer}}$ range from 10 to 20 g/L), the DLS results revealed that the formation of micelle clusters with larger size of $D_h = 600$ –800 nm.

The ζ -potential of PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles as a function of DN is presented in Fig. 5. The absolute ζ -potential gradually increases from -19.4 to -4.5 mV upon increasing DN from 0.4 to 1.0 m, providing an evidence of the progressive neutralization of the anionic PAA blocks of the PAA-*b*-PEO-*b*-PAA by binding the cationic DTAB. The ζ -potential approaches to a constant of -2.0 mV with further addition of DTAB to DN = 2.0. These results are inconsistent with that previously reported complex formed by PEO-*b*-PMA diblock copolymer with various single-tail cationic surfactants [12–15]. In those systems, the ζ -potential approached to zero at DN = 1.0 as the charges of the PMA blocks were neutralized completely. And then it became positive, when DN exceeded 1.0 due to the incorporation of excess surfactants into the complex by hydrophobic interaction between the

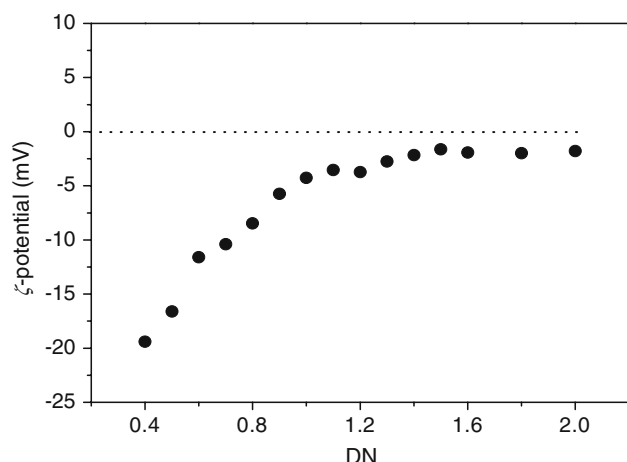


Fig. 5 ζ -Potential of the PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles as a function of the DN at a constant copolymer concentration ($C_{\text{copolymer}} = 1.0$ g/L)

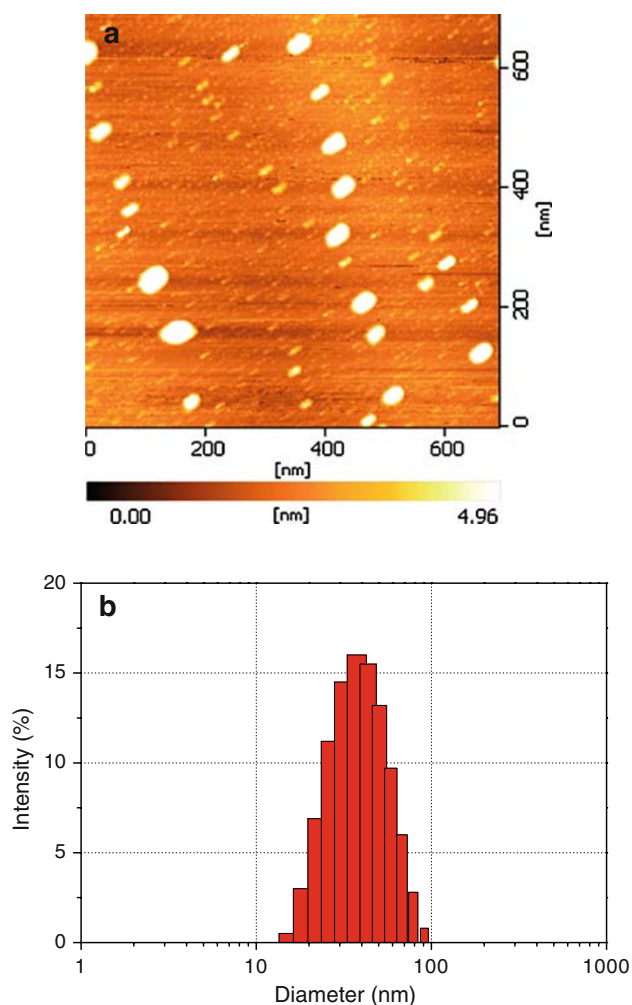


Fig. 6 AFM images (a) and size distribution (b) of the nanoparticles formed by PAA-*b*-PEO-*b*-PAA ($C_{\text{copolymer}} = 1.0$ g/L) and DTAB at DN = 1.1

hydrophobic core of the complex with alkyl chains of surfactants [12–15]. However, in our PAA-*b*-PEO-*b*-PAA/DTAB system, zero ζ -potential was not attained when $\text{DN} > 1.0$, suggesting that the negative charges of the PAA blocks were not neutralized completely. This difference in ζ -potential seems to be attributed to the difference in the structure of the shell of complexes. In the PEO-*b*-PMA/surfactant system, the PEO blocks are grafted on the hydrophobic polyion-surfactant core [12] and extend into the solution to form a loose shell, allowing the excess surfactants to drill through the shell to incorporate with the hydrophobic core. The PEO blocks in the PAA-*b*-PEO-*b*-PAA/DTAB system loop to form a dense shell and the looped PEO blocks hinder the further neutralization of PAA blocks, resulting in some non-neutralized negative PAA-*b*-PEO-*b*-PAA backbones even when $\text{DN} > 1.0$. The sizes and ζ -potential of the PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles remain unchanged for several days in the consequent measurements.

The morphology of the nanoparticles at different DN has been observed with an AFM. A typical AFM micrograph of the nanoparticles formed by PAA-*b*-PEO-*b*-PAA ($C_{\text{copolymer}} = 1.0$ g/L) and DTAB at $\text{DN} = 1.0$ is shown in Fig. 6a. The nanoparticles are in spherical and ellipsoid shapes with diameter from 20 to 40 nm, which agrees well with the DLS results (Fig. 6b).

Conclusions

The novel water-dispersible nanoparticles of double hydrophilic PAA-*b*-PEO-*b*-PAA triblock copolymer binding with DTAB were prepared in aqueous solution at pH 9.0 as the result of the neutralization of anionic PAA blocks and cationic DTAB. The spherical and ellipsoid shaped nanoparticles with a core-shell micellar-like structure, in which the core was formed by the DTAB neutralized PAA blocks and the shell was formed by the looped PEO blocks, were formed in the DN range from 0.4 to 2.0. The ζ -potential of these nanoparticles remained negative over the whole DN range. This is attributed to the structure characters: the looped PEO blocks in the shell of the PAA-*b*-PEO-*b*-PAA/DTAB complex hinder the further neutralization of the PAA blocks with cationic DTAB, resulting in existence of some negative charged PAA-*b*-PEO-*b*-PAA backbones even when $\text{DN} > 1.0$. The stable PAA-*b*-PEO-*b*-PAA/DTAB nanoparticles with average size of 43 ± 3 nm were prepared by simply mixing the triblock copolymer with DTAB in aqueous medium of $C_{\text{copolymer}}$ range from 0.5 to 3.0 g/L at $\text{DN} = 1.0$.

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